

Contaminant Surrogate Evaluation
Subtask 3.1.5

Dioxin is one of the primary risk-driving contaminants in the Lower Passaic River. Dioxin laboratory analysis turn-around time can take up to 21 days. During remedial dredging, immediate feedback will be needed to determine compliance with near-field and far-field water quality criteria. A surrogate contaminant for dioxin or an alternative analytical method with a much shorter turn-around time (preferably < 24 hrs), is needed to provide more immediate feedback during dredging. A surrogate contaminant should have similar release profile, i.e., change of water column concentration with time, as dioxin during sediment disturbance. The release profile of a contaminant is regulated by its concentration in the sediments as well as its desorption rate from sediment particles to water column. Therefore, for a chemical to serve as an appropriate surrogate for dioxin, its concentrations must be correlated to dioxin in the sediments that will be removed, and its desorption rate must approximate that of dioxin as well. Existing Lower Passaic River data for water column and surface sediment were examined to see the correlation between dioxin and other contaminants. A literature review of desorption rates for various contaminants was performed to evaluate potential contaminant surrogates. In addition, a consultation with technical experts, such as Dr. Donald Hayes (University of Nevada, Las Vegas), was also pursued. This task will help to determine if an appropriate surrogate can be used for monitoring contaminant releases during dredging, using an analyte other than dioxin. Note that dioxin will still be analyzed as part of the monitoring program but its analysis requires several days of laboratory work.

In this memorandum, we evaluated the correlations between 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) and other contaminants based on the existing water column and surface sediment data in the Lower Passaic River. The memorandum reviewed the studies on desorption of contaminants from resuspended sediments, focusing on kinetic parameters (i.e., the rates and fractions of contaminant release) and its relationship to the physiochemical properties of the sediments and contaminants. These sources of information were used to identify an appropriate surrogate for 2,3,7,8- TCDD. Release rates were also considered in establishing allowable dredging resuspension [release] rates at near-field and far-field monitoring stations for use during the period of implementation of the Selected Remedy.

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1. Introduction

During dredging, immediate feedback to dredgers is needed to determine compliance with near-field and far-field criteria for allowable release. Because dioxin, one of the primary risk-driving contaminants in the Lower Passaic River, has a long laboratory turnaround time (up to 21 days), a surrogate contaminant or an alternative analytical method, if it exists, for dioxin is needed to provide timely information to assess dredging compliance.

Sediment disturbance can lead to changes in the chemical properties of sediment that stimulate the mobilization of contaminants. The sediments can release contaminants to the water phase in two ways: (1) chemicals in bottom sediment can desorb into pore water and subsequently diffuse/release into overlying waters and (2) bottom sediment particles may be resuspended into the water column and desorption of chemicals can occur. The direct contribution from the pore water is negligible for metals and is low for dissolved organic compounds, unless there is a substantial contribution of dissolved organic matter - bound organic compounds in pore water ¹⁻⁴. Desorption from particles is the most important potential source of dissolved contaminants in the water column ⁵. This desorption process is known to be a limiting kinetic process ⁶⁻⁸, which depends on the desorption rates of contaminants as well as their concentrations in the sediments. Therefore, for a chemical to serve as an appropriate surrogate for dioxin, its concentrations must be correlated to dioxin in the sediments that will be removed, and its desorption rate must approximate that of dioxin as well. In this memorandum, we evaluated the existing surface sediment data in the Lower Passaic River to identify contaminants which had strong correlations with 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). We also summarized the studies on desorption of contaminants from resuspended sediments. The literature data were used to identify contaminants which have similar desorption rates as dioxin.

Different types of contaminants are expected to show different behaviors during sediment disturbance events. Metals, organic and organo metallic contaminants exhibit different affinities for the various solid-phase fractions of sediment. The majority of metal contaminants partition onto particulate matter such as clay minerals, iron and manganese oxides/hydroxides, carbonates, and organic substances ⁹. Organic and organometallic contaminants preferentially partition to organic matter in sediment and dissolved organic matter in pore water ². Contaminants also react differently to the changes in dissolved oxygen, redox potential (Eh) and pH during sediment disturbance events ^{2, 10}. As a result, the behavior of organic compounds and metals during sediment resuspension are discussed separately in the sections below.

2. Hydrophobic Organic Contaminants

This section summarizes the literature data on the desorption kinetics of hydrophobic organic contaminants (HOC) during sediment disturbances as well as the correlation analysis on the existing water column and surface sediment data in the Lower Passaic River.

The release rate of HOC during sediment disturbance is generally described by a specific kinetic model. Section 2.1 gives a brief summary on the kinetic models which were developed based on experimental data. We conclude that the triphasic model is most appropriate to model the release of HOC from resuspended field sediments. Since the triphasic model is characterized by three first-order rate constants and two fractions, sections 2.2 and 2.3 summarize the literature values on the first-order rate constants and desorbing fractions; Section 2.4 discusses the possibility or time interval for the regeneration of the fast or slow desorbing fractions, which can in turn increase the amount of HOC released during a series of sediment disturbance events. Section 2.5 summarizes the effects of physicochemical properties of the sediments and contaminants on desorption rate constants and desorbing fractions. Section 2.6 summarizes the correlation analysis between 2,3,7,8-TCDD and the other contaminants in water column and surface sediment. This information can be used as a basis to select a suitable surrogate compound for 2,3,7,8-TCDD.

2.1 Overview of kinetic models

The desorption kinetics of HOC was generally described by a biphasic desorption model (fast and slow) ^{6, 11-12}, a triphasic desorption model (fast, slow and very slow) ¹³⁻¹⁵, or by diffusion kinetic models ¹⁶⁻¹⁷.

The biphasic desorption model, also known as two compartment model, describes the desorption process as an initial “fast” reaction and a subsequent “slow” reaction. The desorption rate constants are calculated for both fast and slow reactions. The two reactions are also described as reversible and resistant or labile and non-labile. The triphasic desorption model includes a very slow desorption reaction in addition to the fast and slow reactions. The biphasic or triphasic behavior is related to heterogeneity of sediment organic matter. The fast desorbing reaction is associated with the outer sphere of the organic matter, the slow desorbing reaction is associated with bulk amorphous organic matter whereas the very slow desorbing fraction is associated with microcrystalline or condensed-phase organic matter ^{12, 18}. The fast desorbing reaction and desorbing rates typically decrease with sediment aging ^{15, 19}. Therefore, the biphasic model is mostly applicable to laboratory spiked sediments, while the triphasic model is mostly applicable to aged field sediments. The biphasic desorption model can be characterized by two first-order rate constants and one fraction. Similarly, the triphasic model can be characterized by three first-order rate constants and two fractions. The primary disadvantage of the biphasic or triphasic model is the difficulty of relating the kinetic parameters to known properties of sediments. Consequently, these models require recalibration for each type of sediment ¹⁶.

Diffusion kinetic models assume that mass transfer of organics across the sediment–water interface is instantaneous, and their non-equilibrium sorption–desorption kinetic behaviors are the result of time-dependent solute transport between intraparticle pores and interparticle pores within the sediment. Diffusion models usually include detailed geotechnical information of sediments, such as grain size, porosity and density. The models also require chemical

composition information of sediments, including percent organic carbon (f_{oc}) and concentrations of HOC by size fraction, as well as the physical and chemical properties of HOC. For example, the radial diffusion model proposed by Wu and Gschwend indicated that a single effective diffusivity parameter could be used to quantify the sorption/desorption kinetics of HOC. The effective diffusivity could be predicted from compound solution diffusivity, octanol-water partition coefficient (K_{ow}), and sediment organic content, density of water and porosity¹⁶.

Diffusion kinetic models are generally believed to be more conceptually correct; however, the resultant complexity of these models limits their applicability. Therefore, desorption behaviors of HOC from contaminated sediments based on the biphasic and triphasic models are described in this memorandum.

2.2 Desorption rate constants

Desorption rates of HOC from resuspended sediments can be derived from laboratory desorption studies using spiked sediments^{14, 19-21} or field-contaminated sediments^{6, 13-15, 22-23}, or measured in the field, although limited field measurement of the desorption rate was available¹¹. Desorption rates derived from field measurements are generally slower than those obtained from laboratory desorption studies by conventional gas-stripping desorption techniques¹¹. Desorption rates derived from laboratory studies using field-contaminated sediments are also generally slower than the laboratory spiked sediments^{13, 15, 18-19}. Therefore, desorption rates developed from laboratory desorption studies using field-contaminated sediments or from field measurements are more representative of in river dredging or capping activities, and are summarized below and in Table 1.

Field-contaminated sediments in general have undergone different degrees of aging, and contain a small fast desorbing fraction. Desorption of HOC from field-contaminated sediments are generally described by a triphasic model. For studies which used a biphasic model for field-contaminated sediments, the fast (or labile) and slow (resistant) fractions and rate constants actually correspond to the slow and very slow fractions from a triphasic model. To summarize the data in a consistent manner, the kinetic data from the biphasic model were matched to the triphasic model data.

As summarized in Table 1, desorption rate constants for PCDD/Fs from River Kymijoki sediment in Finland were reported to be on the order of 10^{-1} h^{-1} (per hour) for the fast fraction, 10^{-2} h^{-1} for the slow fraction and 10^{-4} to 10^{-6} h^{-1} for the very slow fraction¹⁵. Desorption rate constants for the other HOCs, including PCBs and PAHs, are on the same order as PCDD/Fs (Table 1). Desorption rate constants for PCBs from Hudson River sediments ranged from $(8.5 \text{ to } 33) \times 10^{-3} \text{ hr}^{-1}$ (per hour) for the slow (labile) fraction and $2 \times 10^{-4} \text{ hr}^{-1}$ for the very slow (resistant) fraction⁶. Similarly, desorption rate constants for PCBs from Lake Ketelmeer sediment in Netherlands were reported to be on the order of 10^{-1} h^{-1} for the fast fraction, 10^{-3} h^{-1} for the slow fraction and 10^{-4} h^{-1} for the very slow fraction^{13, 18}.

The desorption rate constant for PAHs during the disposal of contaminated sediments in the coastal environment ranged from $(7 \text{ to } 35) \times 10^{-4} \text{ h}^{-1}$ for the slow fraction ¹¹. The desorption rate constants for PAHs for dredged sediments from Milwaukee Harbor were reported to be on the order of 10^{-2} h^{-1} for the slow (labile) fraction and 10^{-4} to 10^{-5} h^{-1} for the very slow (resistant) fraction ²⁴. The desorption rate constants for PAHs from Indiana Harbor Canal sediments ranged from $(2.5\text{-}7.2) \times 10^{-2} \text{ h}^{-1}$ for the slow (liable) fraction and $(1\text{-}6) \times 10^{-4} \text{ h}^{-1}$ for the very slow (resistant) fraction ⁷⁻⁸. Desorption rate constants for PAHs from Lake Ketelmeer sediment in Netherlands were reported to be on the order of 10^{-1} h^{-1} for the fast fraction, 10^{-3} h^{-1} for the slow fraction and 10^{-4} h^{-1} for the very slow fraction ^{13, 18}.

In general, the fast, slow, and very slow fractions have rate constants on the order of 10^{-1} to 1 h^{-1} , 10^{-2} to 10^{-3} h^{-1} , and 10^{-4} to 10^{-6} h^{-1} , respectively. Considering the wide range of chemical properties for these HOC (PCBs, PAHs, PCDD/Fs) and different sediment types, the variability of desorption rate constants is insignificant, suggesting that desorption rate constants are independent of sediment and HOC properties. Using these general rate constants, the time required for fast fractions to be desorbed is on the order of hours, but the time required for the slow and very slow fractions to be desorbed is on the order of days and years, respectively.

2.3 Fast and slow desorbing fractions

To estimate the extent of HOC desorption from resuspended sediments during dredging or capping, the fast and slow desorbing fractions should be estimated. The very slow desorbing fraction will only take effect if the disturbance lasts for years. Therefore, the fast and slow desorbing fractions will be used along with their corresponding rate constants and sediment residence time to estimate the extent of HOC desorption during sediment dredging or capping.

Table 1 summarizes the literature values for the desorbing fractions. Some studies directly reported the extent of desorption at specified time intervals. For example, about 22% of PCBs were desorbed from the resuspended Hudson River sediment after 2 hours, 35% was desorbed after 2 days, and 55% - 76% was desorbed after 7 days ⁵⁻⁶. About 50% of PCBs were desorbed from Lake Ontario sediments after 40 days ²⁵. About 22% of DDT, 58% of DDD, and 75% of DDE were desorbed from the resuspended Indian Creek sediment after 46 days ²². About 9-18%, 10-41%, 23-50% and 74-91% of PAHs were desorbed from Indiana Harbor Canal sediment after 24 hours, one week, one month, and one year, respectively ⁷⁻⁸. More than 50% of PAHs were desorbed in 51 days upon disposal of contaminated sediment in the coastal environment ¹¹. It is difficult to apply the above desorbing fraction data to the project site because the time interval for the sediment resuspension would be different from the above studies.

The fast desorbing fraction has been estimated as the amount desorbed at 24 hours ²⁶ or at 6 hours ¹⁵ for field sediments. However, some studies have shown that neither of these two periods (6 or 24 hours) were suitable for the fast desorbing fraction ^{8, 27}, rather, the desorbing fractions should be derived from a complete desorbing curve instead of at specified time intervals. By fitting the desorbing curve with a triphasic/biphasic model, it was reported that sediment from Lake Ketelmeer in Netherlands was comprised of less than 5% of the fast

desorbing fraction, approximately 10% of the slow desorbing fraction, and more than 80% of the very slow desorbing fraction for PCBs and PAHs ¹³. River Kymijoki sediment in Finland was comprised of 0.6 to 8% of the fast desorbing fraction, 0.7 to 5.7% of the slow desorbing fraction, and 81 to 99% of the very slow desorbing fraction for PCDD/PCDFs ¹⁵. The fast desorbing fraction for PAHs was less than 5% in the contaminated sediment upon disposal in the coastal environment ¹¹. The fast desorbing fractions for PAHs with $\log_{10}(K_{ow}) > 6$ were in the range of 8 to 10% for Newtown Creek sediments and 25 to 36% for Piles Creek sediment ²⁶.

The distribution of contaminants into fast, slow and very slow fractions is likely affected by sediment size, chemical composition as well as the hydrophobicity of HOC as discussed in Section 2.5. In general, field contaminated sediments are reported to contain a small fast desorbing fraction for HOC with $\log_{10}(K_{ow}) > 6$. After very long contact times (decades) between contaminants in water and sediments, sediment may consist mainly of a very slow desorbing fraction ²⁸.

2.4 Repartitioning

It is assumed that the fast, slow and very slow desorption fractions are associated with distinct physical sites within the sediment matrix. Repartitioning of contaminants between those different domains following depletion of the fast/slow desorption fractions is possible and may occur over the course of months. Chemical repartitioning may occur via direct migration from one domain to the other or through an intermediary phase such as inter- and intra-particle pore water. The repartitioning can lead to regeneration of the fast or slow desorption fractions. The extent of repartitioning is expected to be related to the sediment and chemical properties. The repartitioning of PAH in Indiana Harbor Canal sediments was reported to occur after one month, and were nearly complete after three months ⁸. The repartitioning of PCBs in Hudson River sediment was reported to occur after 4 days for easily desorbed low molecular weight, di-, tri-, and tetra-chlorinated congeners ($\log_{10}(K_{ow}) \leq 5.85$), but not for congeners with $\log_{10}(K_{ow}) > 5.85$ ⁵. The data suggest that the recharge of HOC with $\log_{10}(K_{ow}) > 6$ into fast and slow fractions likely occurs on the time scale of weeks. Reducing the time interval between resuspension events would limit the amount of contaminant released into the dissolved phase.

2.5 Factors affecting desorption rate

Desorption rates of HOC may be affected by sediment properties (particle size, total organic carbon, chemical composition), contaminant properties (thermodynamic properties, chemical planarity or size of molecules) and environmental factors (temperature). The data in the literature do not show a consistent relationship between desorption parameters and the suspected chemical and physical properties of sediment and contaminants or environmental factors as summarized in the following sections.

2.5.1 Sediment properties

2.5.1.1 Organic matter

Organic matter is a predominant sorbent of HOC and is the most essential constituent for the chemicals' sorption/desorption behavior. Not only the amount of organic matter, but also the structure of organic matter should be taken into consideration. It has been suggested that the fast desorbing fraction is associated with the outer sphere of the organic matter and the slow desorbing fraction is associated with amorphous organic matter, whereas the very slowly desorbing fraction is associated with microcrystalline or condensed-phase organic matter¹⁴. The data in the literature do not show a consistent inverse relationship between desorption parameters and organic matter concentration in sediments. This may be related to the different structures of organic matter and other physical properties of the sediments.

Some studies reported a positive correlation between the slow or very slow desorbing fractions of PCB/PAHs and total organic carbon in sediments^{6, 26}, other studies reported that slow and very slow desorbing fractions and corresponding rate constants for PCBs were not correlated with organic matter in sediments²¹. Based on a review of twelve studies, it was concluded that there were not any relationships between fast or slow desorption rate constants of HOC (including PAHs, PCBs, chlorinated benzenes [CB]) and sediment organic matter concentration⁷⁻⁸.

2.5.1.2 Particle size

Sediment properties, such as organic matter, specific surface area, porosity and geotechnical features, vary with particle size. Therefore, desorption parameters are expected to differ among different size ranges of sediment particles if sediment properties are the limiting parameters for desorption kinetics.

The data in the literature are conflicting on the relationships between desorption parameters and particle size distribution. Some studies have shown greater desorption in the fine fractions^{17, 24}, while others have shown greater desorption in the coarse fractions²⁶ or have not observed any particle size dependence⁶.

Effect on rate constants

Ghosh et al. reported that the fast desorption rate constants for fluoranthene and pyrene for coarse lighter-density coal derived particles (63-250 μm) were on the same order of magnitude as that of fine heavier-density clay/silt particles (<63 μm) of dredged sediments from Milwaukee Harbor²⁴. Shor et al. reported that the observed diffusivity and thus the desorption rate constants for PAHs with $\log_{10}(K_{ow}) > 6$ in the coarse (63-125 μm) fractions were about two orders higher than that in the fine (<63 μm) fractions of Newtown Creek and Piles Creek sediments²⁶. Wu and Gschwend reported that the fast and slow desorption rate constants for CBs in the fine (mean aggregate size 96 μm) fractions were about an

order of magnitude higher than that in the coarse (mean aggregate size 232 μm) fractions of Charles River sediments ¹⁶.

Effect on desorbing fractions

Ghosh et al. reported that the fast desorbing fraction for fluoranthene and pyrene in the fine clay/silt particles (<63 μm) was 94%, while it was only 9% in the coarse coal-derived particles (63-250 μm) for dredged sediments from Milwaukee Harbor ²⁴. Based on a radial diffusion model calculation, Wiberg et al. reported that p,p'-DDE was rapidly desorbed from the finest size fractions (<20 μm) in the active bed layer during any resuspension event, whereas only a few percent of the contaminant mass associated with the coarsest size fractions (> 63 μm) in the bed was lost even after the longest resuspension events ¹⁷. Wu and Gschwend reported that the fast desorbing fraction of CBs in the fine (mean aggregate size 96 μm) sediments was 44%, which was slightly smaller than 67% reported for the coarse (mean aggregate size 232 μm) sediments from Charles River ¹⁶. Carroll et al. reported that sediment particle size in the range of <69 μm to 3,327 μm had little impact on the proportion of PCBs remaining after 7 days for Hudson River sediment ⁶.

In summary, the connection between desorption and particle size fraction is not clear for all HOC or sediments, indicating that the mechanism(s) controlling diffusivity or desorption cannot be explained solely by a simple sediment property. Understanding the size-dependence of desorption parameters will help to select the most appropriate model to predict the release of HOC from sediment disturbance.

2.5.2 Contaminant properties

2.5.2.1 Aqueous solubility

Aqueous solubility is the basic thermodynamic measure of chemical potential for mobility in water. Based on a review of twelve studies, it was reported that desorption rate constants for HOC were not correlated with aqueous solubility which ranged over seven order of magnitude (0.0001 – 1000 mg/L). However, the slow release fraction was positively correlated the aqueous solubility⁷⁻⁸.

2.5.2.2 Hydrophobicity

Desorption rate of HOC from suspended sediments is expected to show a trend with their hydrophobicity if diffusion is the limiting process for desorption. Partition coefficients are used to theoretically describe the chemical retardation effect of sediment organic matter during the desorption process. Partitioning behavior of HOC is often described by either a particle-water (K_d), organic carbon-water (K_{oc}), or octanol-water (K_{ow}) partition coefficient. Partition coefficients depend on both contaminants and sediments. It is expected that increased

hydrophobicity (K_{OC} , K_{OW}) leads to higher binding affinity, and thus contributes to slow desorption kinetics.

Effect on rate constant

Inverse dependence of desorption rate constants on K_d , K_{OC} or K_{OW} has been observed for CBs in Charles River sediments¹⁶, for PAHs with $\log_{10}(K_{OW}) > 6$ in Newtown Creek and Piles Creek sediments²⁶, for PCBs in Hudson River sediment⁶, and for PCDD/PCDFs in River Kymijoki sediment in Finland¹⁵. Some studies, however, did not observe any relationship between desorption rate constants and partition coefficients for CBs, PCBs and/or PAHs^{7-8, 13, 21, 25}.

Both sediment properties and contaminant properties are believed to affect the desorption kinetics. Hydrophobicity may be more of the limiting factor for desorption of HOC with $\log_{10}(K_{OW}) > 6$, while sediment properties may be more important for HOC with low hydrophobicity. Additionally, the desorption mechanisms may be different for fast and slow desorption processes. It was reported that for PAHs with $\log_{10}(K_{OW}) < 6$, fast-domain diffusivity was affected by both PAH hydrophobicity and sediment properties, while slow-domain diffusivity was affected by only sediment physicochemical properties²⁶.

Effect on desorbing fractions

The data in the literature show a consistent inverse relationship between fast/slow desorbing fractions (relative to very slow desorbing fraction) and hydrophobicity of HOC^{6-7, 14, 21, 26}, indicating that hydrophobicity of HOC may be important for its distribution among fast, slow and very slow domains in sediment. HOC of high hydrophobicity tends to be more associated with the slow and very slow domains.

2.5.3 Environmental factors

2.5.3.1 Temperature

The Arrhenius relationship was used to describe the effect of temperature on desorption rate or diffusivity²⁴. Desorption rate generally increases with increasing temperature and the magnitude of the increase is related to the active energy. For an activation energy of 120 kJ mol⁻¹, the desorption rate increases by nearly two orders of magnitude as the temperature increases from 10 °C to 37 °C. The activation energy of PCB desorption from Lake Ketelmeer sediment was on the order of 60-70 kJ mol⁻¹ for slow fraction, and 50-60 kJ mol⁻¹ for very slow fraction¹⁴. The activation energy of PAHs (fluoranthene and pyrene) desorption from dredged sediment from Milwaukee Harbor was reported to be from 37 to 41 kJ mol⁻¹ for clay/silt particles and between 133 and 138 kJ mol⁻¹ for coal derived particles²⁴.

The dependence of desorption rate or proportion of easily desorbed fractions on temperature has been reported previously for Hudson River sediment⁶, Lake Ketelmeer sediment¹⁸ and Attachment C

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Lake Ontario sediment ²⁵. Increased temperature enhanced the rate of PCB desorption and significantly increased the labile fraction of PCBs for Hudson River and Lake Ontario sediments. About 35% and 65% of PCBs was desorbed from Hudson River sediment within 24 hours at 20 °C and 100 °C, respectively ⁶. Desorption half-lives of PCBs from Lake Ontario sediments averaged about 60 days at 4°C, 40 days at 20°C and 10 days at 40°C, respectively ²⁵. The desorption rate constants of PCBs for Lake Ketelmeer sediment at 60 °C were about one order of magnitude higher than those at 20 °C, and about two orders of magnitude higher than those at 5 °C. However, the distribution of PCBs among fast, slow and very slow domains was reported to be independent of temperature ¹⁸.

2.6 Correlation Analysis

Existing water column and surface sediment data from Lower Passaic River were analyzed to identify contaminants which showed a strong correlation to 2,3,7,8-TCDD. Figure 1A and Figure 2A provide the linear regression results between 2,3,7,8-TCDD and selected organic compounds in water column and sediment, respectively. The coefficient of determination (R^2) and the number of data points (n) from the linear regression model were used to evaluate their correlations. The results indicate that 2,3,7,8-TCDD in water column has a strong correlation to total PCB, total PAH, total DDD and particulate organic carbon (POC), while 2,3,7,8-TCDD in sediments only shows a strong correlation to total PCB.

2.7 Summary and Implication

The extent of desorption of HOC during a sediment disturbance event is controlled by desorption rate constants, the distribution of HOC among fast, slow and very slow domains, and the residence time of particles in the water column. In general, the time required for fast fraction to be desorbed is on the order of hours, but the time required for the slow and very slow fractions to be desorbed is on the order of days and years, respectively. Riverine particles during dredging are likely not suspended into the water column long enough for desorption of the very slow fraction to contribute significant amounts of dissolved contaminant. Therefore, the fast and slow desorbing fractions are important parameters controlling the extent of desorption. The distribution of contaminants into fast, slow and very slow fractions is likely affected by sediment size, chemical composition as well as the hydrophobicity of HOC as discussed in Section 2.5. For HOC with $\log_{10}(K_{ow}) > 6$, the fast and slow desorbing fractions are generally less than 10%, whereas the very slow desorbing fraction is generally higher than 80% for field aged sediments (Table 1).

2, 3, 7, 8-TCDD is characterized by low water solubility and high lipophilicity. Liquid phase water solubility was reported in the range of $1.59\text{E-}05$ to $5.69\text{E-}04$ mol m^{-3} at 293 to 299 °K and $\log_{10}(K_{ow})$ value was reported in the range of 6.18 to 7.7 ²⁹. Because of these physicochemical properties, the release of TCDDs into water column during sediment resuspension is limited. It was reported that about 81-99% of PCDD/PCDFs in River Kymijoki sediment in Finland was in the very slow desorbing fraction ¹⁵. PCBs may be the most appropriate surrogate for TCDDs

based on their similar physiochemical properties and their strong correlations in the surface sediments.

The desorption fractions discussed above are based on laboratory desorption studies using field sediments, which are typically higher than those measured directly in the field ¹¹. Limited field pilot studies have quantified the fraction of HOC release during sediment dredging events. At Deposit N in the Lower Fox River, less than 2.5% of the PCB mass removed from the bed was released to the water column (dissolved plus suspended) by dredging ³⁰. At the Grasse River, about 3% of the PCBs removed from the river bottom were released downriver, largely (approximately 75%) as PCBs that had desorbed from resuspended sediments ³¹. At the Hudson River site, releases of PCB were dependent on flow conditions and ranged between 0.9% and 7.4% of total mass during Phase I dredging ³² and between 0.2% and 4.3% of total mass during Phase II dredging ³³.

3. Metals

Copper, mercury and lead are contaminants of concerns at the site. This section evaluates the correlation between 2,3,7,8-TCDD and these three metals in water column and surface sediment. We also summarize the literature data on the amounts and time scales of the metal release during sediment disturbance events.

3.1 Mechanism of Metal Release

The mechanism of metal release is different from HOC. The release of HOC is mostly a mass transfer process, while the release of metals is initiated by oxidation of reduced phases (metal sulfides) during sediment disturbance.

Metals are often bound to a variety of sediment fractions ranging from exchangeable, carbonate, oxide and sulfide/organic matter phases. In most anoxic sediments, sulfides are considered the predominant solid phases controlling the concentrations of the metals, including copper, iron, manganese, lead, mercury and zinc. Upon resuspension of sediment into an oxic overlying water, several competing reactions can occur:

- (1) Oxidation of metal sulfides, thereby producing oxidized sulfur species, and releasing the associated metal to the water column.
- (2) Oxidation of iron and manganese, thereby causing the precipitation of iron and manganese oxyhydroxides. The released metal can be quickly adsorbed or co-precipitated with these oxyhydroxides.
- (3) Metals adsorbed or co-precipitated with iron and manganese oxyhydroxides can be further released into water column by reaction with hydrogen ion.
- (4) Released metals can be complexed by organic matter and remain relatively stable in the water phase.

Based on the above release mechanism, the release of metals is related to the binding forms of heavy metals in the sediments, the amount of iron and manganese in the sediments, the acid neutralization capacity of the sediments, as well as the relative affinity of dissolved metals to iron and/or manganese oxyhydroxides and/or dissolved organic matter (DOM).

The rate of oxidation of iron and manganese is faster than sulfide oxidation, therefore, the amount of heavy metals present will probably show a shift from precipitated mode (metal sulfides) to the adsorbed mode (metals co-precipitated with iron and manganese oxyhydroxides) during sediment disturbance. If pH remains relative constant around 7, the release of metals would be negligible. If pH changes below 4, the release of metals would be significant through the third reaction pathway listed above.

3.2 Release Profile

Resuspension of oxic sediments did not lead to a substantial release of metals³, while during aeration of anoxic sediments with high acid volatile sulfide concentrations, metals usually desorbed quickly, but were then followed by re-adsorption^{3, 34}.

Following resuspension of anoxic sediment in aerated seawater over a period of 80 days, the maximum dissolved phase concentrations of iron and manganese occurred <1 hour after exposure of the sediments to seawater. Their concentrations then decreased rapidly over the following 2 to 3 weeks³. Following resuspension of anoxic sediment in aerated deionised water over a period of 76 days, aluminum, iron and lead had the maximum concentrations at day 1 and became undetectable after 14 days. Mercury had the maximum concentration at day 1 and became undetectable after 3 days. Manganese was not detected in solution during the whole experiment, while copper increased steadily³⁴. The increase of copper is mainly related to its ability to be complexed by DOM, and therefore, the re-adsorption rate is slower.

Often the release of metals during sediment disturbance is small due to the adsorption or co-precipitation with iron and manganese oxyhydroxides. During the resuspension of anoxic sediments, the releases of metals were reported to be small and the order of contaminant release was found to be as Cd (5%) > Zn (1.5%) > Cu (1%) > Pb (0.7%) over a period of 25 days³⁵. Similarly in another study, the order of contaminant release was reported as Zn (0.50%) > Cu (0.29%) ~ Pb (0.29%) > Hg (0.06%) > Fe (0.05%) > Al (0.02%) > Mn (0%) over a period of 76 days³⁴. No release of Zn, Cu, Cd, and Pb was observed during a field pilot study of dredging contaminated anoxic sediment with relatively high sulfide levels for a period of 7 hours⁴. However, Shipley et al. reported a larger release of metals following resuspension of anoxic sediment over a period of 6 days. The fraction of metals released from sediments followed the order of Mn (62.6%) > Cd (58.2%) > Zn (57.6%) > Co (36.5%) > Ni (21.2%) > Cu (3.6%) > As (1.2%) > Pb (0.35%) > Fe (0.03%). The larger release of metals is mainly attributed to the change of pH in water. The pH decreased from 7.2 to 3.8 during Shipley's study, while it remained relatively constant around 7.5 during the other studies^{4, 34}. When calcite was added to control the pH, Shipley also reported no or little release of metals.

3.3 Correlation Analysis

Existing water column and surface sediment data from Lower Passaic River were analyzed to identify metals which showed a strong correlation to 2,3,7,8-TCDD. Figure 1B and Figure 2B provide the linear regression results between 2,3,7,8-TCDD and selected metals (i.e. lead, copper and mercury) in water column and sediment, respectively. The coefficient of determination (R^2) and the number of data points (n) from the linear regression model were used to evaluate their correlations. The results indicate that 2,3,7,8-TCDD in water column has a strong correlation to copper, lead and mercury, while 2,3,7,8-TCDD in sediments does not show correlation to these metals.

3.4 Implication

As discussed above, the release of metals is mainly caused by oxidation of anoxic sediments (mainly metal sulfides). The oxidation rates of FeS, FeS₂ and MnS are reported to be faster than other metal sulfides including CdS, Cu₂S, PbS, ZnS and HgS. During sediment disturbance, FeS and MnS phases (usually present in large excess to other metal sulfides) may buffer the effects of disturbance and that trace metal sulfide phases may remain predominantly unoxidized for some time. Metals which have strong affinity to iron or manganese oxyhydroxides, such as lead, could minimize their release to the aqueous phase. On the other hand, metals which have stronger complexing capacity of DOM, such as copper, could result in a relatively higher release.

Sediment's acid neutralization capacity plays another important role in the release of metals. The oxidation of metal sulfides causes a pH decrease, which may result in a very rapid transfer of a substantial fraction of the metals in the adsorbed iron or manganese oxyhydroxides phase to the free mode. Sediments of higher neutralization capacity can buffer the acidification process and prevent the release of metals.

The pH is expected to remain unchanged during dredging or capping in the lower 8.3 miles of the Lower Passaic River, therefore, the fractions of metals, including copper, lead and mercury, released from sediments to the overlying water are likely less than 1%. In summary, metals are not appropriate surrogates for 2,3,7,8-TCDD due to their different physiochemical properties and lack of correlations to 2,3,7,8-TCDD in the surface sediments.

4. Conclusions and Recommendations

In summary, the release of 2,3,7,8-TCDD from sediments into the water column is expected to be low because of its high hydrophobicity. Since the turnaround time for dioxin analysis is longer than required for management decisions to be made on dredging and capping related issues, an appropriate surrogate is needed. Organic compounds which have similar hydrophobicity as 2,3,7,8-TCDD, such as PCBs, can be suitable surrogates to monitor the release

of 2,3,7,8-TCDD. In addition, PCBs are collocated with 2,3,7,8-TCDD in the sediments that are targeted for dredging and are also correlated in the existing baseline water column observations. Furthermore, extensive experience on the Hudson River indicates that laboratory turn-around time for PCBs could be as rapid as 24 hours. While the release of metals, including mercury, lead and copper is also expected to be low, metals are not good surrogates for 2,3,7,8-TCDD due to their different chemical characteristics, release mechanisms and lack of correlation to 2,3,7,8-TCDD in the sediments. Even if a good surrogate is identified, some dioxin analysis will still be required initially at the beginning of the remedial action to ensure that relationships developed between dioxin and the surrogate during the design continue to remain valid during active remediation.

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